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Joel M. Bowman

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Skirting the transition state, a new paradigm in reaction rate theory

Joel M. Bowman*

Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, GA 30322

In this issue of PNAS, Houston and Kable (1) describe experiments that implicate a new mechanism for chemical reactions in the photodissociation of acetaldehyde. The “roaming” mechanism was discovered in a recent combined experimental/theoretical study of formaldehyde photodissociation (2, 3). (Formaldehyde is acetaldehyde with the methyl group replaced by hydrogen.) This mechanism is a reaction pathway that bypasses the conventional transition state of the reaction. It has major consequences for experimental observations in the case of formaldehyde photodissociation, and its explication solved a puzzle brought to the attention of researchers in the field by an important paper on formaldehyde photodissociation by van Zee *et al.* in 1993 (4).

The measurement, prediction, and understanding of the rates of chemical reactions are of fundamental importance in chemistry and chemical biology. Since its inception more than 75 years ago, transition state theory (TST) has been both the conceptual foundation and the predictive tool for the theory of reaction rates (5–7). Today, computer codes (8) based on this theory and important refinements to it, for example, to approximately include quantum mechanical tunneling, are in widespread use. Attempts to develop fully quantum versions of TST have also been pursued (9). The fundamental ideas of TST were incorporated into statistical theories of reaction rates 55 years ago by Marcus (10) into what is now termed RRKM theory (for Rice, Ramsperger, Kassel, and Marcus).

TST makes quantitative the earlier concept of the activation energy of a chemical reaction. It does so by identifying a feature of the potential energy surface that governs the nuclear motion in a chemical reaction with this activation energy. For many reactions, this feature is an energy barrier (mathematically, a saddle point) that separates the reactants and products and nuclear motion that transforms the reactants into the products must pass over (or possibly tunnel through) this saddle point. For obvious reasons, this point is also called the TS, and from its local properties, the temperature dependence of the absolute reaction rate can be calculated.

It would not be an exaggeration to state that TST is the theory of reaction

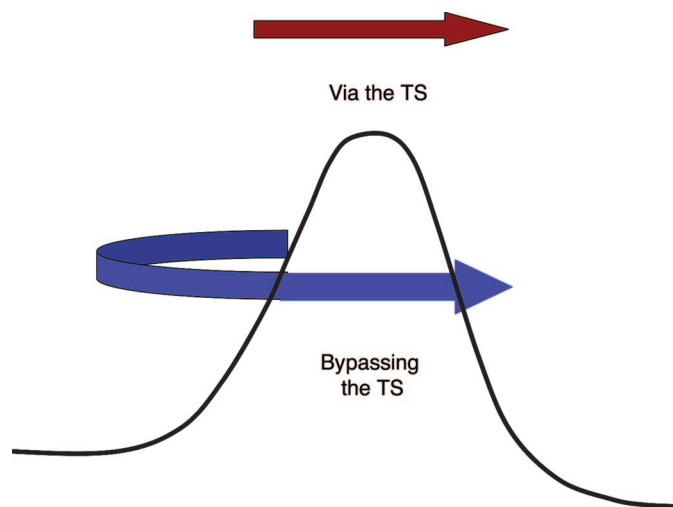


Fig. 1. Depiction of the usual “textbook” reaction. Proceeding from left to right, shown are reactants to products by the energetic TS and a second pathway that bypasses that barrier.

rates. It has been validated for many years and will continue to be used in the future. Thus, it came as a surprise when recent experiments and calculations on the photodissociation of formaldehyde (H_2CO) clearly demonstrated that the molecular products of this reaction, $\text{CO} + \text{H}_2$, are also formed by a pathway that skirts the well defined TS. The experimental and calculated signature of this second path is remarkably clear: the

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H_2 product is formed vibrationally highly excited, whereas it is only slightly excited when the reaction follows the path over the saddle point (2, 3). The calculations indicate that the second pathway commences with a single H atom separating from H_2CO and entering the $\text{H} + \text{HCO}$ dissociation channel. However, instead of separating into those products, the incipient $\text{H} - \text{HCO}$ fragments execute a fairly complex motion that results in “self reaction,”

where the nearly free H atom abstracts the H atom in HCO to form the molecular products, $\text{H}_2 + \text{CO}$. In this abstraction pathway, these products emerge with very different internal energies than from the TS pathway, H_2 is very highly vibrationally excited, and CO is rotationally cold, whereas the opposite is found when the reaction takes the TS pathway. Animations of several of these non-TS pathway trajectories (see supporting information, which is published on the PNAS web site) have led to the characterization of this unusual pathway as the “roaming H atom.”

Houston and Kable (1) report another likely example of the “roaming” pathway in the photodissociation of CH_3CHO . In this case, it is the methyl radical that may be roaming about the HCO fragment and abstracting the H atom to form vibrationally excited CH_4 (and rotationally cold CO). By contrast, the CH_4 molecular product formed by the TS is not vibrationally very excited, but the CO product is rotationally excited. In addition to these signatures of two pathways, Houston and Kable (1) report another

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See companion article on page 16079.

*E-mail: jmbowma@emory.edu.

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striking signature of the second pathway, the lack of significant alignment of the CO molecular rotation relative to the velocity vector of the separating CH₄ and CO products. This implies that the abstraction of the H atom in HCO by the CH₃ fragment occurs at a variety of relative orientations. By contrast, rotationally excited CO (presumably formed by the conventional TS) is aligned, i.e., the CO angular momentum vector points in the direction perpendicular to the relative velocity vector; this is consistent with the known TS configuration. Stimulated by this observation, we reexamined H₂CO trajectories and indeed found substantial rotational alignment of rotationally excited CO formed by the conventional molecular TS, which is planar, but very little alignment for rotationally cold

CO, accompanied by vibrationally hot H₂ (J. Farnum and J.M.B., unpublished work), in qualitative agreement with the Houston and Kable (1) results for CH₃CHO (Fig. 1).

In summary, the work reported by Houston and Kable (1) and the earlier work on H₂CO pointing to a roaming mechanism in reaction dynamics demonstrate dramatic deviations from conventional TS dynamics. Skirting the TS need not require a roaming hydrogen atom, although examples to date have been restricted to that. Other studies, perhaps less dramatic than the roaming ones, also point to reaction dynamics that are either not dominated by a TS or that appear to occur without passing through an obvious TS (11–15). For example, in a combined experimental/theoretical paper, Marcy *et al.* (11) ob-

served that the CO+H+H₂ products from the reaction CH₃+O do not apparently form by a conventional TS but instead occur in a stepwise fashion from reaction intermediates. In other work on the H+HBr (12) and H+CH₄ reactions (13–15) at high energies, it was found that the reactions proceed by pathways that deviate substantially from the conventional TS, with consequences that are experimentally measurable. Thus, there is mounting evidence that, although TS theory is still a robust theory of reaction rates, other reaction mechanisms that bypass the TS or do not involve a TS are possible and indeed may be ubiquitous. The work by Houston and Kable (1) adds significantly to this evidence and will certainly stimulate calculations to fully interpret and help understand their fascinating experiment.

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